Experimental report

02/04/2021

Proposal: **CRG-2506** **Council:** 4/2018

Title: Pressure effect on the quantum rotations of encaged methane

Research area:

This proposal is a new proposal

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Samples:
CH4
methane hydrate (D2O-CH-4)

Instrument	Requested days	Allocated days	From	To
IN6-SHARP	5	5	20/06/2018	25/06/2018

Abstract:

This experiment was initially aimed at investigating the effect of high pressure on the rotational dynamics of methane molecules encaged in methane clathrate hydrate at low temperature. The focus of the experiment had to be modified due to technical issues. High-pressure pure methane (CH_4) was measured instead of high-pressure methane hydrate (CH_4+H_2O). Measurements were performed at 300±1 K. During the assigned 5 days of beamtime, we measured spectra of methane at the following ten pressures: 0.12, 0.16, 0.23, 0.28, 0.29, 0.40, 0.50, 0.81, 1.13, and 1.44 GPa.

Two high-pressure setups were employed to cover a wide pressure range up to the freezing pressure. For the measurements up to 0.5 GPa, we used a cylindrical pressure cell of aluminium alloy whose internal diameter was 6 mm. A cylindrical aluminium spacer of 5.5 mm in diameter was inserted to reduce the multiple scattering contributions and fluid methane was contained in the resulting hollow circular cylinder. The sample pressure was changed using a gas compressor working with methane. No piston or separator was used; methane filled the sample chamber as well as the capillary connecting the compressor with the cell. The acquisition time was typically 3-4 hours per pressure point.

A VX5 Paris-Edinburgh press was employed to collect data up to 1.44 GPa. In this setup, a quasi-spherical 50 mm^3 sample is encapsulated inside a metallic gasket and squeezed between two anvils. We used a copper-beryllium gasket and anvils made of zirconia-toughened alumina ceramics. The clamp module of the Paris-Edinburgh press was inserted into a high-pressure vessel and methane was loaded at room temperature and 0.2 GPa. The employed gas compressor and high-pressure vessel are installed at the ILL. Approximately 30 mm^3 of $Na_2Ca_3Al_2F_{14}$ powder was loaded in the sample chamber to reduce multiple scattering and to serve as a pressure gauge. Acquisition times ranged between 6 and 12 hours per pressure point.

The self-diffusion coefficient of methane turned out to be $3.69\times10^{-9} m^2 s^{-1}$ at 1.44 GPa and 300 K, a value that is comparable to that of liquid methane at ambient pressure and 100 K from the literature. We found that the high-pressure behaviour of the diffusion coefficient along the room temperature isotherm departs from that expected for a dense fluid of hard spheres and suggests a density-dependent molecular diameter. Breakdown of the Stokes–Einstein–Sutherland relation was observed. A fractional Stokes–Einstein–Sutherland relation correctly represents the data over their entire range of pressures with a power-law exponent of 0.73±0.02, namely a value very far from that of the Lennard–Jones fluid (0.92). These findings underpin the lack of a simple model for predicting the pressure dependence of the diffusion coefficient of dense fluid methane. We found that the quantity $D\eta/\rho$ remains constant within 10% in our experimental results along the 300 K isotherm (D being the diffusion coefficient, η the shear viscosity, ρ the density). These results have been recently published [1].

Reference

[1] U. Ranieri, S. Klotz, R. Gaal, M. M. Koza, and L. E. Bove, "Diffusion in dense supercritical methane from quasi-elastic neutron scattering measurements." Nature Communications, 12, 1958 (2021).